

both Type A and Type B, was synthesized. Through further refinement, Type A and Type B carbonate apatite can be selectively synthesized, and the degree of substitution of carbonate ions for the phosphate ions in Type B carbonate apatite can be controlled. Important parameters will be reaction and aging temperatures, carbonate source, method of carbonate introduction, precursor concentrations, aging time, and pH.

SUMMARY OF EXAMPLES

The above examples demonstrate superior processes and products resulting from densifications of nanocrystalline hydroxyapatite. The grain sizes of calcined samples varied from 30 nm to 100 nm depending how pH, aging time, reaction and aging temperature, $\text{Ca}(\text{NO}_3)_2$ addition rate, precursor concentration, and grinding method were controlled, while the grain sizes of conventional hydroxyapatite were on a micron scale. For example, the surface area of one sample of the invention after calcination at 550° C. is 159.5 m²/g while the conventional sample after calcination at 550° C. has a very small surface area of 5.4 m²/g. The sample of the invention retained phase uniformity after calcination at 550° C., but the conventional sample began to transform into tricalcium phosphate at 550° C. with substantial conversion to tricalcium phosphate and calcia by 700° C. In a sample of the invention 96% of the theoretical density was obtained at a low sintering temperature of 1100° C. by pressureless sintering for nanocrystalline hydroxyapatite which was stable up to 1300° C. However, the conventional sample achieved only 70% of the theoretical density at 1200° C. with decomposition into tri-calcium phosphate. Furthermore, the densified conventional sample contained large pores and microcracks. Our nanocrystalline hydroxyapatite has high purity and phase homogeneity as well as superior sinterability compared to the conventionally prepared hydroxyapatite. When our nanocrystalline hydroxyapatite was sintered using either colloidal or hot pressing, 99% theoretical bulk density with a grain size of less than 250 nm can be obtained. Dense nanocrystalline hydroxyapatite compacts further possessed a compressive strength as high as 745 MPa, while the conventional micron-sized hydroxyapatite compacts from a similar pressureless sintering treatment possessed a compressive strength of 150 MPa. Additionally, further reinforcement of the hydroxyapatite can be accomplished by introducing a secondary dispersoid such as zirconia which would greatly improve the toughness and chemical stability of hydroxyapatite by pinning the mobility of any intergranular and intragranular defects. A dense composite of nanocrystalline hydroxyapatite and 10 wt % nanocrystalline 3 mol % Y_2O_3 -doped ZrO_2 possessed an even higher compressive strength of 1020 MPa. With more complete characterization, the densified nanocrystalline hydroxyapatite and hydroxyapatite-zirconia composites can easily be developed into dental and orthopedic weight-bearing implants. Furthermore, the processing of nanocrystalline hydroxyapatite can be adapted to synthesize a nanocrystalline carbonate apatite illustrating the versatility of our process. This process can also be used to selectively synthesize Type A and Type B carbonate apatite as well as to control the degree of substitution of the carbonate ion into the apatite structure.

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that actual parameters will depend upon the specific application for which the methods and apparatus of the present invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A composition, comprising particulate apatite having an average apatite crystal size of less than 100 nm, wherein the crystal is spherical.
2. The composition of claim 1 comprising particulate apatite having an average apatite crystal size of less than 50 nm.
3. The composition of claim 1 comprising particulate apatite having an average apatite crystal size of less than 30 nm.
4. The composition of claim 1 comprising particulate apatite having an average apatite crystal size of less than 20 nm.
5. A composition as in claim 1 wherein the particulate apatite is densified.
6. The composition of claim 1 comprising apatite having an average particle size of less than 1 μm .
7. The composition of claim 1 comprising apatite having an average particle size of less than 0.5 μm .
8. The composition of claim 1 comprising apatite having an average particle size of less than 0.25 μm .
9. A composition comprising particulate apatite having a surface area of at least 40 m²/g and a spherical crystal.
10. The composition of claim 7 comprising particulate apatite having a surface area of at least 100 m²/g.
11. The composition of claim 9 comprising particulate apatite having a surface area of at least 150 m²/g.
12. The composition of claim 9 that undergoes apatite phase decomposition of less than 10% when exposed to conditions of at least 1000° C. for at least 2 hours.
13. The composition of claim 12 that undergoes apatite phase decomposition of less than 5% when exposed to conditions of at least 1000° C. for at least 2 hours.
14. The composition of claim 12 that undergoes apatite phase decomposition of less than 3% when exposed to conditions of at least 1000° C. for at least 2 hours.
15. The composition of claim 12 that undergoes apatite phase decomposition of less than 10% when exposed to conditions of at least 1100° C. for at least 2 hours.
16. The composition of claim 12 that undergoes apatite phase decomposition of less than 5% when exposed to conditions of at least 1100° C. for at least 2 hours.
17. The composition of claim 12 that undergoes apatite phase decomposition of less than 3% when exposed to conditions of at least 1100° C. for at least 2 hours.
18. The composition of claim 12 that undergoes apatite phase decomposition of less than 10% when exposed to conditions of at least 1200° C. for at least 2 hours.
19. The composition of claim 12 that undergoes apatite phase decomposition of less than 5% when exposed to conditions of at least 1200° C. for at least 2 hours.
20. The composition of claim 12 that undergoes apatite phase decomposition of less than 3% when exposed to conditions of at least 1200° C. for at least 2 hours.

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21. The composition of claim 12 that undergoes apatite phase decomposition of less than 10% when exposed to conditions of at least 1300° C. for at least 2 hours.

22. The composition of claim 12 that undergoes apatite phase decomposition of less than 5% when exposed to conditions of at least 1300° C. for at least 2 hours.

23. The composition of claim 12 that undergoes apatite phase decomposition of less than 3% when exposed to conditions of at least 1300° C. for at least 2 hours.

24. An article having a dimension of at least 0.5 cm made up of the composition of claim 1.

25. The article of claim 24 wherein the particulate apatite is consolidated.

26. The article of claim 24, formed into the shape of a prosthesis.

27. The article of claim 24 that is a prosthesis.

28. The article of claim 24 comprising an exterior coating on a prosthesis.

29. The article of claim 28 comprising an exterior coating, on a prosthesis, of at least 0.5 micron in thickness.

30. The article of claim 24 having a theoretical density of at least 90%.

31. The article of claim 24 having a theoretical density of at least 95%.

32. The article of claim 24 having a theoretical density of at least 98%.

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33. An article having a dimension of at least 0.5 cm made up of the composition of claim 9.

34. The article of claim 33 having a porosity of at least 20%.

35. The article of claim 33 having a porosity of at least 30%.

36. The article of claim 33 having a porosity of at least 50%.

37. The article of claim 33 having a porosity of at least 75%.

38. The densified article of claim 33 having compressive strength of at least about 150 MPa.

39. The densified article of claim 38, having a density of at least about 98%.

40. The densified article of claim 33 having compressive strength of at least about 500 MPa.

41. The densified article of claim 33 having compressive strength of at least about 700 MPa.

42. The densified article of claim 38, having a density of at least about 90%.

43. The densified article of claim 38, having a density of at least about 95%.

44. The article of claim 24 that is a part of a prosthesis.

no
a.

no
b.

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